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First examples of gold nanoparticles catalyzed silane alcoholysis and silylative pinacol coupling of carbonyl compounds

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Abstract

In this Letter, we illustrate the first catalytic application of supported Au nanoparticles in silane alcoholysis. The reaction proceeds with low amount of catalysts, under solvent free conditions for liquid substrates, without additional ligands and in a very selective way for primary alcohols in the examined cases. Additionally, a gold catalyzed silylative pinacol coupling of carbonyl compound is observed for the first time and some hypotheses about the reaction mechanism are given.

Keywords: Gold nanoparticles; Catalysis; Hydrosilanes; Alcoholysis; Pinacol coupling

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Since the discovery of the catalytic activity of gold nanoparticles in low temperature CO oxidations,[1] there has been an explosion in the interest shown in catalysis by gold. A number of reviews have recently been reported regarding the applications of supported Au nanoparticles,[2–4] Au(I) and Au(III) salts or complexes,[4,5] as catalysts in several reaction of interest such as oxidations, hydrogenations, additions and so on, indicating the versatility of such systems. As relevant examples, Au(I) or Au(III) complexes, and also a supported Au/CeO_2 systems are reported to be efficient catalysts for the hydrosilylation of carbonyl compounds to the corresponding silyl ether.[6–8]

It has been recently shown that supported Au nanoparticles obtained by metal vapourization are very active catalysts for terminal alkynes hydrosilylation in heterogeneous phase.[9] Following this finding, we investigated the use of supported gold catalysts in reactions involving hydrosilanes. In particular, we focused our attention on silane alcoholysis (Scheme 1). Silyl ether (**1**, Scheme 1) formation is not only a fundamental process in the synthesis of functional organosilicon compounds but also an important technique for the protection of reactive hydroxy groups during multistep organic syntheses.[10] From the standpoint of 'green chemistry',[11] this transformation should be conducted through catalytic dehydrogenative silylation with a hydrosilane rather than through electrophilic silylation with a silyl electrophile ($R_3Si–X$) in combination with a stoichiometric base.[12] The former produces H_2 as the sole byproduct instead of a base–HX salt in the latter. Several metal complexes have successfully been used as selective homogeneous catalysts, including Ir(I),[13] Cu(I)[14] and also Au(I)[15] systems. In all these cases, complex organic ligand and 0.5–1% loading of metal catalyst are used to obtain good performances. Classical heterogeneous catalysts, such as Pd/C or Raney Ni are very active in this reaction, but scarcely chemoselective.[12] Recently, an interesting heterogeneous version of the reaction was

$$\mathrm{ROH} \;+\; \mathrm{R'_3SiH} \longrightarrow \underset{\mathbf{1}}{\mathrm{ROSiR'_3}} \;+\; \mathrm{H_2}$$

Scheme 1.

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reported, in which a perfluorinated dirhodium(II) complex adsorbed on silica resulted in a very efficient and reusable catalyst under solvent free conditions.[16] To our knowledge, no example of heterogeneous gold catalyzed silane alcoholysis has been reported.

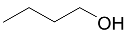
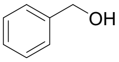
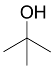
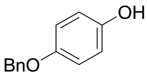
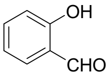
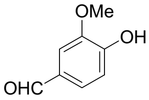
For our tests we used Au/Al_2O_3 catalysts with 1% metal loading prepared in two different ways: metal vapour synthesis[17] (Au_{MVS}) and deposition–precipitation method[18] (Au_{DP}). Both catalysts contain small Au nanoparticles (3–5 nm of mean diameter), but it has been reported that in Au_{MVS} the gold is essentially zerovalent, while the metal surface of clusters is largely oxidized to Au(I) in Au_{DP}.[19] Our results of silane alcoholysis of various alcoholic substrates are reported in Table 1.[20,21]

Entries 1–4 show that, for *n*-butanol, excess Et_3SiH increases reaction rate, but in any case $PhMe_2SiH$ is a better choice than Et_3SiH. Both Au_{MVS} and Au_{DP} catalysts show practically the same activity. We generally used conditions of entry 4 as optimized conditions for the other substrates. With liquid substrates (entry 1–6), reactions were carried out in the absence of solvent. Under the selected conditions, the reaction proceeds smoothly only with primary alcohols of the analyzed series (entries 4–7), demonstrating high chemoselectivity in these cases. *tert*-Butanol is recovered practically unreacted after 3 h of reaction. If the reaction time is prolonged to 18 h, we observe 55% of *tert*-butanol conversion, but a complex mixture of unidentified products is obtained. After the same prolonged time, the conversion of the electron-rich phenol (entry 7) in the corresponding siloxane is only 5% in toluene. The use of a reaction solvent in the case of solid substrate is needed to have complete dissolution of the substrate. The reaction rate proved to be greatly influenced by this parameter (entries 7–9). For 4-benzoyloxyphenol (entries 7–9), refluxing THF seems to be the better choice but the reaction is still very slow. Salicylaldehyde is recovered unchanged after 18 h (entry 10). The same reaction, carried out with vanillin, provided a complex mixture of products with 74% conversion in 18 h (entry 11). To investigate in more detail the influence of the presence of a CHO group on the outcome of the reaction, we performed a series of trials using benzaldehyde as the substrate.

Hydrosilylation of carbonyl compounds using Au(I) or Au(III) complexes, and also a supported Au/CeO_2 system was reported to afford the corresponding silyl ether in good yields.[6–8] Surprisingly, we obtained the silylated pinacol coupling product **3** (Scheme 2) together with the expected silylalcohol **2** using our gold catalysts, as shown in Table 2.[22]

In most of the cases, the main product is **3** (meso/dl = 50:50) instead of the expected **2**. In particular, Au_{MVS} catalysts with $PhMe_2SiH$ afford **3** with a 80:20 selectivity both for benzaldehyde and acetophenone (entries 2 and 4), while Au_{DP} catalysts give predominantly the expected

Table 1
Gold catalyzed silane alcoholysis of various substrates

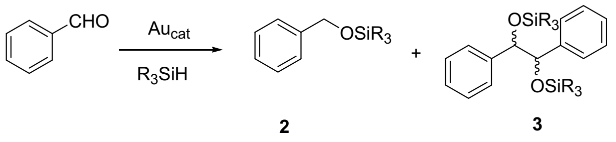
Entry	Alcohol	Silane	Cat	Solvent/*T*/time	Conversion[a]
1		Et_3SiH	Au_{MVS} 0.05%	—/100 °C/18 h	82%
2		Et_3SiH[b]		—/100 °C/6 h	76%
3		$PhMe_2SiH$		—/100 °C/3 h	95%
4		$PhMe_2SiH$	Au_{DP} 0.05%	—/100 °C/3 h	99% (92%)
5		$PhMe_2SiH$	Au_{DP} 0.05%	—/100 °C/3 h	99% (95%)
6		$PhMe_2SiH$	Au_{DP} 0.1%	—/100 °C/3 h	<1%[c]
7		$PhMe_2SiH$[b]	Au_{DP} 0.05%	Toluene/110 °C/3 h	<1%[d]
8				1,4-Dioxane/100 °C/18 h	49%
9				THF/65 °C/18 h	50% (44%)
10		Et_3SiH	Au_{MVS} 0.1%	—/100 °C/18 h	<1%
11		$PhMe_2SiH$	Au_{MVS} 0.1%	Toluene/110 °C/18 h	74% mixture of products

[a] Determined by GC analysis; where not specified, **1** is detected as the sole product. In parenthesis, isolated yield of the product purified by column chromatography (SiO_2, hexane/AcOEt 4:1).

[b] Silane/alcohol = 2.

[c] 55% conversion after 18 h, complex mixture of products.

[d] 5% conversion in silyl ether **1** after 18 h.



Scheme 2.

silylalcohol **2**, with 60:40 selectivity, if $PhMe_2SiH$ is used (entry 3). These findings suggests that the oxidation state of gold could govern the product distribution: Au(I) species may favour the classical hydrosilylation reaction, while Au(0) species may favour the pinacol-type coupling. Accordingly, if the Au_{DP} catalyst is pre-treated with the silane for 1 h at 100 °C before the addition of aldehyde (reducing conditions), the selectivity is still switched to the predominant formation of **3** (**2**:**3** = 38:62). From a mechanistic point of view, we can suppose that Au(I) may favour an addition–elimination mechanism, while Au(0) can act as a radical initiator which affords pinacol-type coupling products with a meso/dl ratio of 50:50, by analogy with reported mechanisms.[8,23] A plausible mechanism is depicted in Scheme 3.

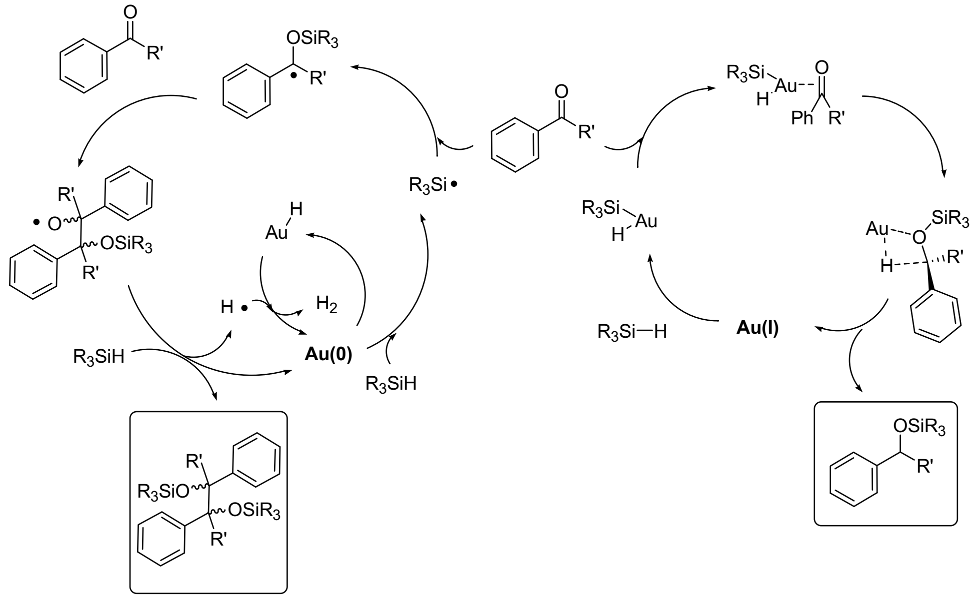
Finally, we tested other functionalized substrates in the reaction with $PhMe_2SiH$ under optimized conditions, namely decylamine, dodecanethiol and methyl benzoate. No reaction occurs in all these cases.

In this Letter, we illustrated the first catalytic application of supported Au nanoparticles in silane alcoholysis. The reactions proceed with low amount of catalysts (0.05% with respect to alcohol), under solvent-free conditions for liquid substrates, without additional ligands and in a very selective way for primary alcohols in the examined cases. Since supported Au nanoparticles have proven to be ineffective in hydrosilylation of some other functionalized compounds, such as alkenes[7], amines, thiols and esters, this procedure seems to be suitable for the selective protection of primary alcohols, or the synthesis of silyl ethers, in the presence of various functionalities. Further investigation is in progress about this opportunity. Moreover, the use of low amounts of a supported catalysts (easier to recover than homogeneous systems) and the absence of additional ligand and solvents, make this reaction very promising. In addition, we observed for the first time a gold catalyzed silylative pinacol coupling of carbonyl compound and gave some hypotheses about the reaction mechanism. Further

Table 2
Au/Al_2O_3 catalyzed hydrosilylation of carbonyl compounds

Entry	Silane	Cat	Solvent/T/time	Conversion[a]	Selectivity[a] 2:3
1	Et_3SiH	Au_{MVS} 0.1%	—/100 °C/18 h	95% (32%)	36:64
2	$PhMe_2SiH$	Au_{MVS} 0.1%	—/100 °C/18 h	96% (50%)	20:80
3	$PhMe_2SiH$	Au_{DP} 0.1%	—/100 °C/18 h	77%	60:40
4[b]	$PhMe_2SiH$[c]	Au_{MVS} 0.15%	—/100 °C/24 h	99%	20:80

[a] Determined by GC. In parenthesis, isolated yield (not optimized) of product **3** purified by column chromatography (SiO_2, hexane/AcOEt 4:1).
[b] Acetophenone used as substrate instead of benzaldehyde.
[c] Silane/ketone = 2.



Scheme 3. Plausible mechanisms for gold catalyzed hydrosilylation and silylative pinacol coupling.

studies are required to define the scope of this new reaction and to confirm the mechanistic suggestions. In conclusion, a new reactivity for gold nanoparticles is shown, that we hope could disclose new ways in gold catalyzed organic reaction research.

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20. All reactants and reagents were purchased from Sigma–Aldrich and used without further purification. GC analyses were performed with a DB1 capillary column (30 m × 0.52 mm, 5 μm) using He as the carrier gas and a flame ionization detector (FID). ^{1}H NMR spectra were recorded with a Gemini 200 MHz instrument, in $CDCl_3$ solution using $CHCl_3$ as internal standard. The metal content in the catalysts was determined by atomic absorption spectrometry in an electrochemically heated graphite furnace with a Perkin–Elmer 4100ZL instrument, after the dissolution of the solid in hot aqua regia.
21. *General experimental procedure*: Catalytic runs of solvent free reactions have been carried out in Pyrex Carius tubes fitted with Rotaflo taps. Reactions in solution were carried out in a two-necked round flasks, equipped with refrigerator and magnetic stirrer. Under inert atmosphere, to the indicated amount of Au/Al_2O_3 were added via syringe 2 mmol of alcohol, 2 or 4 mmol of silane and, when present, the reaction solvent. The suspension was stirred for a chosen time at the reported temperature, filtered on Celite and the filtrate analyzed by GC analysis. The formation of 1 was confirmed by comparison with GC of authentic samples, obtained by standard procedure ($R_3SiCl/Et_3N/DMAP/CH_2Cl_2$).
22. *General experimental procedure*: Same as Ref. 21. Product **3** (meso/dl = 50:50) for entry 1 was characterized by GC–MS and ^{1}H NMR analysis. GC–MS: *m/z*, (rel. int.) = 413 (M^+−29, 1); 221 (99). H NMR (200 MHz, CDCl3): 0.6–1.1 ppm, 30H, multiplet; 4.8 ppm, 1H, singlet; 4.9 ppm, 1H, singlet, 7.1–7.5, 10H, multiplet.
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